520 Rec'd PCT/PTO 02 NOV 1999

FORM PTO-1390 (REV 11-98)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
FILED: NOVEMBER 2, 1999
306.37599X00

U S APPLICATION NO (If known see 37 CFR 1 5)
09/423086

INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP98/02562	30 April 1998 (30.04.98)	02 May 1997 (2.05.97)

TITLE OF INVENTION
REDUCTION OF HARMFUL GASES IN GAS MIXTURES FROM PYROTECHNIC REACTIONS

APPLICANT(S) FOR DO/EO/US
BLEY, Ulrich; RIEDECKER, Klaus; REICHELT, Martin; and WEUTER, Waldemar

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND or SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [X] A change of power of attorney and/or address letter.
16. [X] Other items or information:
    International Publication No. W098/50324
    PCT Request Form
    International Preliminary Examination Report
    Figure 1

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U.S. APPLICATION NO (if known see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUUMBER
09/423086	PCT/EP98/02562	306.37599X00

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5))

	CALCULATIONS	PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$970.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$840.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$760.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$670.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$96.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 840.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(c)).	$ 0.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	10 -20 =	0	X $18.00	$ 0.00	
Independent claims	5 -3 =	2	X $78.00	$ 156.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+$260.00	$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				$ 996.00	
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also by filed (Note 37 CFR 1.9, 1.27, 1.28).				$ 0.00	
SUBTOTAL =				$ 996.00	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0.00	
TOTAL NATIONAL FEE =				$ 996.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 0.00	
TOTAL FEES ENCLOSED =				$ 996.00	
				Amount to be: refunded	$
				charged	$

a. [X] A check in the amount of $ 996.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. ________ in the amount of $________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-2135 A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Alan E. Schiavelli
Antonelli, Terry, Stout & Kraus, LLP
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SIGNATURE

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NAME

32,087
REGISTRATION NUMBER

09/423086

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: BLEY et al

Serial No.:

Filed: November 2, 1999

For: Reduction of Harmful Gases In Gas Mixtures From Pyrotechnic Reactions

Group:

Examiner:

PRELIMINARY AMENDMENT

Assistant Commissioner
for Patents
Washington, D.C. 20231

November 2, 1999

Sir:

Prior to examination on the merits of this application and prior to calculation of the filing fee, please amend the above-identified application as follows:

IN THE CLAIMS:

Claim 3, line 3, delete "or 2".

Claim 6, line 2, delete "or 5".

Claim 7, line 2, delete "one of claims 4 to 6" and insert --claim 4--.

Claim 9, line 1, after "generation" insert --according to claim 8--.

Claim 10, line 1, after "generation" insert --according to claim 8--.

REMARKS

The foregoing amendments are respectfully requested prior to examination on the merits of this application.

To the extent necessary, applicants petition for an extension of time under 37 CFR 1.136. Please charge any shortage in the fees due in connection with the filing of this paper, including extension of time fees, to the deposit account of Antonelli, Terry, Stout & Kraus, LLP, Deposit Account No. 01-2135 (Case: 306.37599X00), and please credit any excess fees to such deposit account.

Respectfully submitted,

ANTONELLI, TERRY, STOUT & KRAUS, LLP

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1/PRTS

09/423086

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Reduction of harmful gases in gas mixtures from pyrotechnic reactions

The present invention relates to the reduction of harmful gases in gas mixtures from pyrotechnic reactions.

An airbag system has, as basic components, impact sack, gas generator and trigger device which initiates an electric ignition in the gas generator as required, when a previously specified triggering threshold is exceeded. As a result, a gas is generated within a very short time (approx. 40 ms, depending on the airbag module), and flows into an air sack which spreads out between the passengers in the vehicle and the site of impact. The gas-producing substance (expanding agent, propellant) used is a solid mixture of fuel, oxidizing agent and additives in the form of tablets, which reacts within the combustion chamber in about 10 to 40 ms after ignition has taken place.

For gas generation, as the gas-producing substance, (expanding agent, propellant), sodium azide (NaN_3) has hitherto chiefly been used as the fuel . The great advantage of azide generators is that the gas liberated consists of nitrogen to the extent of almost 100 per cent and therefore is not a health risk. Because of the high toxicity of sodium azide (LD_{50} value of 27 mg/kg), which is comparable to that of potassium cyanide (cyanide of potassium), however, with further use the problems of disposal and recycling of airbag gas generators in resulting scrap vehicles and the hazards and risks of criminal misuse would become ever greater.

Possible alternative substances are organic nitrogen-rich compounds, which achieve good performance values (gas yield, pressure course etc.) similar to those of

sodium azide. Extensive studies and analyses by the Applicant have shown that 5-aminotetrazole is suitable as an environment-friendly alternative fuel. The result was an expanding agent of 5-aminotetrazole, oxidizing agents and additives, which is called SINCO.

When the alternative solid fuels such as 5-aminotetrazole burn up, in addition to the non-toxic working gases nitrogen, carbon dioxide and water vapour, amounts of the toxic gases carbon monoxide, nitrogen monoxide and nitrogen dioxide are formed.

An object of the present invention has therefore been to achieve minimization of the harmful gas concentrations when the alternative solid fuels are employed.

Formation of NO (all types) is in general favoured at higher temperatures and longer residence times of the gases and waste gases in the high temperature range. The processes known hitherto in the prior art for reducing the amount of nitrogen oxide are chiefly based on lowering the combustion temperature. Additional thermal formation of NO is prevented by rapid cooling of the waste gases. However, the low combustion temperatures have the disadvantage that they increase the formation of CO. Non-uniform combustion processes can lead to marked formation of both harmful gases. Local or brief overheating thus causes the formation of NO, and local or brief undercooling causes the formation of CO.

An alternative for suppressing NO is combustion in catalyst-coated pores or capillary spaces. Catalytic combustion processes are very low in harmful substances, but also sensitive with respect to the operating conditions and require expensive catalyst materials.

The object underlying the invention has been solved by introduction of substances into the flow path of the working gas, for example by coating components of the gas generator. The substance introduced is vaporized here by the heat of combustion, which, in a homogeneous gas phase reaction, has the effect of converting the harmful gases into non-toxic compounds.

The substances to be employed according to the invention for reducing the amount of nitrogen oxides for use in airbag gas generators must meet the following requirements:

- Non-toxic
  → Problems during disposal or recycling are thus avoided.

- Melting point > 105°C
  → In strong sunlight, the airbag module can be heated up to 105°C. It must be ensured that the additive does not liquefy and be discharged from the airbag module in such a case. Only substances having a melting point > 105°C are therefore suitable.

- Vaporization below 400°C
  → At the places in the gas generator where the additive is to vaporize, temperatures no higher than 400°C are to occur due to the rapid cooling of the gas.

- Long-term stability (15 years)
  → A gas generator should be fully functional over the entire life of a car (up to 15 years).

- No danger to health from the gases formed
  → The gases liberated during the vaporization should not be a health hazard and also should undergo no reactions which lead to toxic compounds.

- Effect of reducing the amount of nitrogen oxides
  → The substance introduced should have the effect of reducing the nitrogen oxides in a homogeneous gas phase reaction.

- Inexpensive

These criteria are met by the following substances, which can be classified into three groups (Table 1).

Metallocenes and their derivatives	*Urea and urea derivatives*	*Sulphur and sulphur compounds*
ferrocene 1,1'-diacetylferrocene titanocene pentasulphide	Urea N-formylurea N,N'-dimethylurea N,N-dimethylurea	sulphur (titanocene pentasulphide)

Table 1: Overview of the substances employed

The experiments were carried out in an apparatus which allows measurement of the variation of concentration with respect to time of nitrogen monoxide and nitrogen dioxide in a reaction container of 60 l capacity.

The flow diagram of the process in the test apparatus is shown in figure 1. It can be divided into the following equipment components:

- the gas feed
- the batch reactor
- the nitrogen oxide analyzer with its auxiliary

units.

The test apparatus substantially comprises the batch reactor of plastics material and the nitrogen oxide analyzer. At the start of each experiment, nitrogen monoxide, which is partly converted into nitrogen dioxide with atmospheric oxygen in an equilibrium reaction, is metered into the reactor. The temperature in the reactor is 45°C in all the experiments. After about 10 minutes, when the nitrogen dioxide concentration scarcely changes further, the particular substance is vaporized in the container. The concentration courses can be determined by regular recording of the values for the nitrogen dioxide and nitrogen monoxide concentration, and these allow conclusions to be drawn regarding the activity of the particular substance.

Results which allow a comparison of substances in respect of their activity in reducing the amount of nitrogen oxides can be obtained with this test apparatus.

The experiments have surprisingly shown:

- A reduction in the nitrogen dioxide concentration was achieved with all the substances tested.

- Ferrocene shows the best action. A rapid degradation of nitrogen dioxide is achieved with comparatively small amounts.

The following experiments are intended to explain the invention without limiting it:

Experimental set-up:

Plastics material was chosen as the material for the reactor in order to avoid reactions which may occur on a metallic wall. The plastics container employed is not very heat-stable. The temperature in the container should therefore not exceed 45°C, so that no deformations of the container wall result. The reactor contains a vaporizer and a fan heater. The vaporizer essentially comprises a heating plate which is continuously temperature-controllable up to 350°C and on which the test substances can be heated to the sublimation or boiling point in a glass dish. The fan heater serves to establish a desired temperature and to thoroughly mix the reaction mixture intensively. Mixing is necessary in order to ensure the same reactant concentrations and temperatures in the entire reactor. The temperature in the reactor can be established and re-adjusted manually with an adjuster connected to the heating of the fan heater. Regulation of the temperature in the container is necessary because of the heat losses via the wall, the heat supplied via the heating plate and the endo- or exothermic reactions which proceed in the reactor. The temperature is measured with a thermocouple connected to a voltmeter.

To measure the concentration of nitrogen oxides (NO, NO_2), a chemiluminescence apparatus is employed, to which the bypass pump, the silica gel drying cartridge and the ozone destroyer/pump unit are also connected. To protect the chemiluminescence apparatus from contamination, a microfibre filter is incorporated between the reactor and the chemiluminescence apparatus.

The nitrogen monoxide is fed in with the aid of a gas bag which, filled beforehand, is connected to the three-way stopcock. The calibrating gas (nitrogen with

80 ppm nitrogen monoxide) is passed directly to the chemiluminescence apparatus from the pressure bottle via a pressure reducer. The gas should flow into the analyzer without pressure. Approx. 50% or 0.6 l/min of the amount of gas required must therefore flow out via a T-piece with an excess line. The excess is passed into a fume cupboard. The excess line has a length of more than 2 m, in order to avoid mixing of the calibrating gas with the air of the atmosphere. A flow meter is also installed on the line, so that the predetermined value for the volume flow can be monitored. Only pipes with a smooth surface and made of inert material, such as PTFE, glass or steel, have been used as the gas lines.

Experimental procedure:

A specific amount of the substance to be tested is weighed into a glass dish and spread uniformly on the glass base. The glass is then placed in the middle of the heating plate and the temperature setting of the vaporizer is checked. Thereafter, the lid is placed on the plastics container and the lever on the clamping ring is pressed closed. The screw fittings on the container connections are now tightened firmly, so that tightness of the container is ensured. The thermocouple is connected to the voltmeter and the lines from the fume cupboard and filter must be connected to the three-way stopcocks of the container lid, which must be set such that the container is closed off. Calibration can take place while the container air is being heated up to 45°C with the fan heater. As soon as the temperature in the reactor has reached 45°C, nitrogen monoxide is metered into the container via a gas bag at three-way stopcock I, this being partly converted into nitrogen dioxide with atmospheric oxygen by an equilibrium

reaction. As soon as there is nitrogen monoxide in the reactor, measurement of the time is started.

The first measurement value is recorded after about 30 seconds and the second after approximately 5 minutes. With the preheating time, which has been determined before the measurement, a time at which the vaporizer is switched on is specified, so that the substance starts to vaporize after approx. 10 minutes. At this time, a state in which the nitrogen dioxide concentration changes only slowly has become established in the plastics container.

Shortly before vaporization of the substance, a measurement value is also read off on the chemiluminescence apparatus and entered into the measurement record. The time intervals between the measurement points after the boiling point has been reached depend on the particular course of the reaction resulting with a certain substance. The measurement values are recorded over a period of 25 - 30 minutes. The temperature in the reactor must be monitored continuously throughout the entire measurement, and, if necessary, re-adjusted manually via an adjuster.

When the measurement has ended, the plastics container must be opened to the ambient atmosphere and must be vented for at least 15 minutes. The tubes, filter, container and three-way stopcocks are then cleaned thoroughly and dried.

Experimental programme:

Three experiments were first carried out without vaporization of an additive. The variation of concentration of nitrogen monoxide and nitrogen dioxide without the influence of a substance converted into the

gas phase could be plotted as a result. Comparison of the values determined experimentally with those calculated theoretically was furthermore possible.

Table 2 shows a summary of the experiments carried out with the additives.

Table 2. Summary of the experiments carried out

Ferrocene			
Amount of substance [g]	0.015	0.0225	0.03
Number of measurements with NO/NO_2 gas mixture	3	3	3
Number of measurements with $NO/NO_2/CO$ gas mixture	-	3	-
1,1'-Diacetylferrocene			
Amount of substance [g]	0.05	0.1	-
Number of measurements with NO/NO_2 gas mixture	3	3	-
Titanocene pentasulphide			
Amount of substance [g]	0.05	0.1	0.15
Number of measurements with NO/NO_2 gas mixture	3	3	3
Urea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
N-formylurea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
N,N'-Dimethylurea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
Number of measurements with $NO/NO_2/CO$ gas mixture	-	3	-
N,N-Dimethylurea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
Sulphur			
Amount of substance [g]	0.05	0.1	0.15
Number of measurements with NO/NO_2 gas mixture	3	3	3
Number of measurements with $NO/NO_2/CO$ gas mixture		3	

It can be seen from Table 2 that with some substances - one substance was chosen from each substance group - the

influence of carbon monoxide gas on the reactions proceeding in the container was additionally also investigated.

Influence of ferrocene on the nitrogen oxide concentrations:

The effects on the nitrogen monoxide and nitrogen dioxide concentrations which result due to vaporization of 0.015 g ferrocene were determined in the test apparatus. In the initial phase of the measurement, the variation of the concentrations with respect to time is as expected. The nitrogen monoxide concentration falls due to oxidation of the nitrogen monoxide with atmospheric oxygen, as a result of which the nitrogen dioxide concentration increases. As soon as the ferrocene is in the gas phase (after 540 s), a steep, virtually linear drop in the nitrogen dioxide concentration starts. It decreases by 40 ppm within 35 seconds. During this period of time, the nitrogen monoxide concentration remains constant at a value of 178 ppm. It then falls further, and the nitrogen dioxide concentration increases again.

To check the 1st measurement, two further experiments were carried with 0.015 g ferrocene and similar nitrogen oxide concentrations. The same variation in concentration as in the 1st measurement is found in each of the two repeat measurements. As soon as the ferrocene is in the gas phase, a rapid drop in the nitrogen dioxide concentrations takes place. In experiment no. 2 this is 39 ppm in 43 s, and in experiment no. 3 it is 45 ppm in 45 s. The nitrogen monoxide concentrations remain at a constant value during this period.

If the amount of ferrocene is increased to 0.0225 g, the drop in the concentration of the nitrogen dioxide gets

bigger. The concentration falls by 90 ppm in 88 s. This approximately corresponds to twice as great a reduction as in the experiments with an amount of 0.015 g ferrocene.

On the other hand, a further increase in the amount of substance to 0.03 g brings no further increase in the lowering of the concentration. The nitrogen dioxide concentration is lowered by 88 ppm within 75 s. The results were in each case confirmed in two further measurements.

The values for the decrease in nitrogen dioxide for all the measurements are summarized in Table 3.

Table 3: Summary of the lowering of nitrogen dioxide by ferrocene in the gas phase

	0.015 g ferrocene	0.0225 g ferrocene	0.3 g ferrocene
Experiment no. 1	40 ppm	90 ppm	88 ppm
Experiment no. 2	39 ppm	70 ppm	80 ppm
Experiment no. 3	45 ppm	82 ppm	83 ppm

The combustion gases of a gas generator also contain amounts of carbon monoxide, in addition to the nitrogen oxides. Three measurements were therefore carried out additionally with carbon monoxide gas, with an amount of 0.03 g ferrocene and the same experimental conditions as in the previous experiments, in order to detect possible influences of carbon monoxide on the results. The ratio of CO to NO_2 in the combustion gases of the gas generator is about 10 to 1. This concentration ratio was established in the reactor. The CO gas content was measured with Dräger tubes (relative standard deviation: ± 10 to 15%). The results show that the variation in the nitrogen monoxide and nitrogen dioxide concentrations does not change with carbon monoxide gas.

The values for the reduction in nitrogen dioxide with and without carbon monoxide are compared in Table 4.

Table 4: Summary of the decrease in nitrogen dioxide without and without carbon monoxide

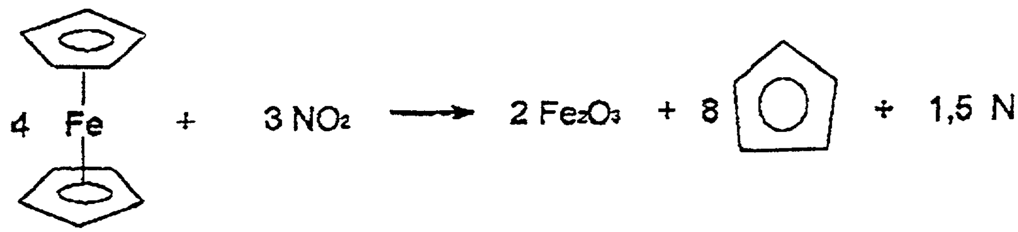
	0.03 g ferrocene (without CO)	0.03 g ferrocene (with CO)
Experiment no. 1	88 ppm	91 ppm
Experiment no. 2	80 ppm	85 ppm
Experiment no. 3	83 ppm	86 ppm

Interpretation of the results:

To be able to explain the results of the experiments with ferrocene, an FT-IR analysis of the residue which forms in the reactor was carried out. For this, the reactor was rinsed out with water after an experiment. The resulting mixture was then evaporated in a rotary evaporator. After the residue which remained had been dried in a drying cabinet, the KBr pellet was prepared for the FT-IR analysis and the analysis was then carried out in an FT-IR apparatus.

In addition to the FT-IR analysis, a GC analysis was also carried out for identification of the gaseous products. For this, 100 mg ferrocene were kept in a headspace glass at 80°C for 2 hours in order to convert some of the ferrocene into the gas phase. Thereafter, 3 ml of an NO/NO_2 mixture were added to the glass. 2 ml of gas from the headspace glass were analyzed in a gas chromatograph. It was found that, in addition to the ferrocene and air constituents, the gas phase also additionally contained cyclopentadiene.

It can be concluded from the above investigations that ferrocene reacts with nitrogen dioxide in a redox reaction to give iron(III) oxide, cyclopentadiene and nitrogen.



The rapid decrease in the nitrogen dioxide concentrations in the experiments can be explained by this equation. The constant nitrogen monoxide values could be attributed to the fact that the nitrogen dioxide is only partly reduced to nitrogen monoxide and the formation and degradation are therefore in equilibrium.

Influence of 1,1'-diacetylferrocene on the nitrogen oxide concentrations:

The variation in nitrogen oxide concentration in an experiment with 0.1 g 1,1'-diacetylferrocene was investigated. Until this substance vaporizes, the concentrations change as expected. The nitrogen monoxide values fall due to oxidation and the nitrogen dioxide values increase. Shortly after the start of the vaporization operation, the nitrogen monoxide concentration increases by 24 ppm in 233 s - initially sharply, then becoming less intense. The nitrogen dioxide concentration similarly falls by 26 ppm. The normal NO/NO_2 equilibrium course is then established again.

The results of the 1st experiment were confirmed in two further measurements with 0.1 g 1,1'-diacetylferrocene. In the 2nd experiment, a decrease in the NO_2 concentration by 23 ppm and an increase in the NO concentration by 25 ppm occurred in 262 s. In a 3rd

experiment, it was found that the NO_2 values fall by 24 ppm and the NO values rise by 23 ppm in 250 s.

When only 0.05 g 1,1'-diacetylferrocene was introduced into the gas phase, it was found that the values for the decrease in nitrogen dioxide and for the increase in nitrogen monoxide were lower by about half compared with the experiments with 0.1 g (Table 5). Qualitatively, however, the courses of the concentrations as a function of time are identical.

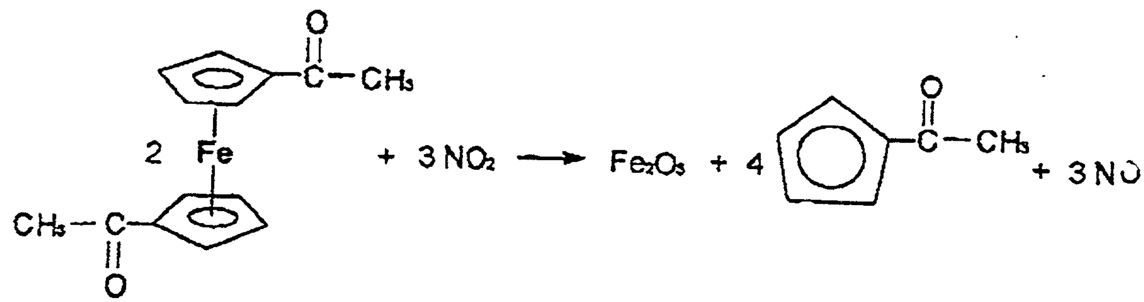
All the results of the experiments with 1,1'-diacetylferrocene are summarized in Table 5.

Table 5: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.05 g 1,1'-diacetylferrocene		0.1 g 1,1'-diacetylferrocene	
	NO	NO_2	NO	NO_2
Experiment no. 1	+13 ppm	-13 ppm	+24 ppm	-26 ppm
Experiment no. 2	+12 ppm	-11 ppm	+25 ppm	-23 ppm
Experiment no. 3	+11 ppm	-11 ppm	+23 ppm	-24 ppm

Interpretation of the results:

It can be seen from Table 5 that a decrease in nitrogen dioxide results in a corresponding increase in nitrogen monoxide. This effect is probably due to a redox reaction of the 1,1'-diacetylferrocene with the nitrogen dioxide, which is accordingly reduced to nitrogen monoxide. Compared with ferrocene, the ferrocene derivative 1,1'-diacetylferrocene is a much poorer reducing agent with the additional disadvantage of the formation of nitrogen monoxide.



Influence of titanocene pentasulphide on the nitrogen oxide concentrations:

The effects on nitrogen monoxide and nitrogen dioxide which result from vaporization of 0.05 g titanocene pentasulphide were investigated. The nitrogen dioxide concentration falls virtually linearly from 253 ppm to 225 ppm in 85 s due to titanocene pentasulphide in the gas phase. In contrast, the nitrogen monoxide concentration increases in the same way from 269 ppm to 298 ppm. Before the vaporization and after the reaction of the titanocene pentasulphide with the nitrogen oxides, the normal variations concentration courses occur, i.e. decrease in the nitrogen monoxide due to oxidation and, as a consequence, an increase in the nitrogen dioxide.

Two further experiments with 0.05 g titanocene pentasulphide led to results similar to those in the 1st experiment. The precise values for the changes in the concentrations can be seen from Table 6, in which all the results of the three measurements are summarized.

Table 6: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.05 g titanocene pentasulphide		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	77	+29	-28
Experiment no. 2	85	+25	-24
Experiment no. 3	76	+23	-26

By increasing the amount of the substance from 0.05 to 0.1 g, the values for the nitrogen monoxide increase and the nitrogen dioxide decrease have approximately doubled. In 103 s, the nitrogen dioxide concentration fell by 50 ppm from 351 ppm to 301 ppm. In the same period of time, the nitrogen monoxide concentration rose by 48 ppm from 306 ppm by 48 ppm to 354 ppm. Two further experiments with 0.1 g titanocene pentasulphide give results which are in agreement, these being summarized in Table 7.

Table 7: Overview of the increase and decrease respectively in the concentrations of NO and NO_2

	0.1 g titanocene pentasulphide		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	103	+48	-50
Experiment no. 2	108	+51	-53
Experiment no. 3	100	+55	-56

An increase in the amount of the substance to 0.15 g had the effect of a further decrease in the nitrogen dioxide and a corresponding increase in the nitrogen monoxide. The nitrogen monoxide concentration rises by 75 ppm in 130 s, and at the same time the nitrogen dioxide

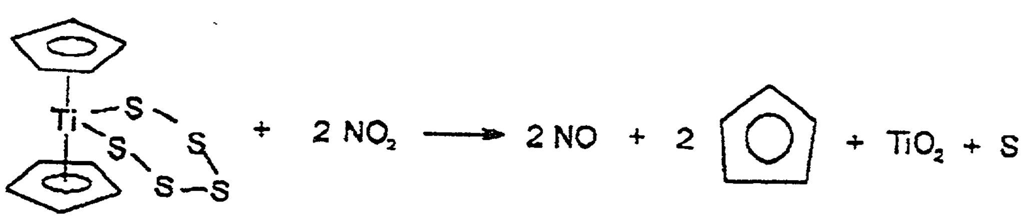
concentration falls by 77 ppm. Comparable results are achieved in the two repeat experiments, which are shown in figures A.19 and A.20 in the appendix (see Table 8).

Table 8: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.15 g titanocene pentasulphide		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	130	+75	-77
Experiment no. 2	115	+70	-68
Experiment no. 3	125	+68	-72

Interpretation of the results:

An FT-IR analysis of the residue which has formed in the reactor should provide information on the reaction mechanism. In the FT-IR spectrum obtained, everything indicates that the residue comprises titanocene pentasulphide and titanium(IV) oxide (TiO_2). There is accordingly very probably a redox reaction of the titanocene pentasulphide with nitrogen dioxide, in which the reaction products cyclopentadiene, nitrogen monoxide, titanium(IV) oxide and sulphur are formed. This explains the simultaneous formation of nitrogen monoxide during the degradation of nitrogen dioxide.



Influence of urea on the nitrogen oxide concentrations:

There are no striking changes in the variation in concentration of nitrogen monoxide when urea is

vaporized in the reactor. In contrast, a decrease in the concentration of nitrogen dioxide from 82 ppm to 54 ppm occurs. This reduction by 28 ppm takes place in 410 s. Thereafter, the nitrogen dioxide values increase again slowly. The two repeat experiments confirm these results. All the results of the experiments with 0.1 g urea are shown in Table 9.

Table 9: Summary of the decrease in the NO_2 concentration

	0.1 g urea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	410	-28
Experiment no. 2	420	-26
Experiment no. 3	470	-32

If 0.4 g urea is employed, the nitrogen dioxide is degraded to a significantly greater extent compared with the addition of 0.1 g urea. In the first 300 s after the start of the vaporization process, a relatively rapid decrease in the nitrogen dioxide concentration takes place. The values then fall further at a decreasing rate. At the end of the measurement, a lowering of the nitrogen dioxide concentration is still detectable. Overall, a reduction in the nitrogen dioxide by 111 ppm takes place in 20 min. All the results which were achieved with 0.4 g urea are shown in Table 10.

Table 10: Summary of the decrease in the NO_2 concentration

	0.4 g urea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	1200	-111
Experiment no. 2	1200	-108
Experiment no. 3	1200	-114

An increase in the amount of urea to 0.7 g leads to even higher values for the decrease in nitrogen dioxide. A reduction in the nitrogen dioxide concentration by 179 ppm in 1,200 s is found. The qualitative variation of the measurement values is otherwise identical to the variation which resulted when 0.4 g urea was employed. The results of the repeat experiments can be seen from Table 11.

Table 11: Summary of the decrease in the NO_2 concentration

	0.7 g urea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	1200	-179
Experiment no. 2	1200	-200
Experiment no. 3	1200	-188

Interpretation of the results:

When urea is heated above its melting point, ammonia (NH_3), which is known as a reducing agent for nitrogen oxide reduction, is formed. It is to be assumed that the degradation of nitrogen dioxide takes place by a homogeneous gas phase reaction of ammonia with nitrogen dioxide. The reduction of the NO_2 with NH_3 can be described by the following overall reaction equations:

Main reactions

$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$

$2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$

Side reaction

$12\ NO_2 + 16\ NH_3 + 7\ O_2 \rightarrow 14\ N_2O + 24\ H_2O$

- Nitrogen (N_2) and water vapour are formed in the main reactions as reaction products of this selective reduction. The undesirable dinitrogen monoxide (N_2O) from the side reaction does not appear to be formed to a substantial extent.

Nitrogen monoxide is slow to react compared with nitrogen dioxide. This could be the reason why the nitrogen monoxide is not reduced with ammonia at a temperature of 45°C.

Influence of N-formylurea on the nitrogen oxide concentrations:

On vaporization of 0.1 g N-formylurea, the nitrogen dioxide concentration starts to fall relatively slowly from the time 750 s to the time 1,230 s. The concentration is reduced from 162 ppm by 12 ppm to 150 ppm during this period. Thereafter, the values remain approximately constant. No striking changes are detectable in the course of the nitrogen monoxide concentration.

All the results achieved in the 3 experiments with 0.1 g N-formylurea are summarized in Table 12.

Table 12: Summary of the decrease in the NO_2 concentration

	0.1 g N-formylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	480	-12
Experiment no. 2	500	-14
Experiment no. 3	450	-14

To investigate the effects on the nitrogen oxides when the amount of the substance is increased, in each case 3 experiments were carried with 0.4 g and 0.7 g N-formylurea.

The nitrogen dioxide concentration falls by 63 ppm in 460 s by vaporization of 0.4 g N-formylurea. Similar results are achieved in the 2nd and 3rd experiment with an NO_2 reduction of 54 ppm and 66 ppm respectively. Table 13 gives a summary of all the results. There are no changes in the qualitative variation in the concentrations compared with the experiments with 0.1 g.

Table 13: Summary of the decrease in the NO_2 concentration

	0.4 g N-formylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	460	-63
Experiment no. 2	480	-54
Experiment no. 3	480	-66

In contrast to the experiments with an amount of the substance of 0.1 g and 0.4 g, the nitrogen dioxide concentration still continues to fall slowly, after a relatively rapid decrease, when 0.7 g N-formylurea is employed. In a chosen period of 1,000 s, a reduction in

nitrogen dioxide by 85 ppm thus results. Two repeat experiments confirm this result (see Table 14)

Table 14: Summary of the decrease in the NO_2 concentration

	0.7 N-formylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	1000	-85
Experiment no. 2	1000	-94
Experiment no. 3	1000	-80

Interpretation of the results:

When N-formylurea is heated above its melting point, ammonia is probably formed. The homogeneous gas phase reactions which take place as a result are the same as those described for urea. N-Formylurea has a higher molecular weight than urea because of the formyl group. As a result, less ammonia is formed with N-formylurea than with urea when the same amounts are vaporized. This explains the poorer values for the reduction of nitrogen dioxide compared with the experiments with urea.

Influence of N,N'-dimethylurea on the nitrogen oxide concentrations:

The influence of 0.1 g N,N'-dimethylurea was investigated. No changes were found in nitrogen monoxide compared with the normal concentration course. In contrast, the content of nitrogen dioxide is decreased by 48 ppm in 465 s. After this decrease, the values for the nitrogen dioxide concentration remain virtually constant to the end of the measurement. The results of all three experiments with 0.1 g N,N'-dimethylurea are shown in Table 15. The results of the repeat experiments show no substantial differences from

the first experiment here.

Table 15: Summary of the decrease in the NO_2 concentration

	0.1 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	465	-48
Experiment no. 2	497	-40
Experiment no. 3	506	-38

The vaporization of 0.4 g N,N'-dimethylurea in the reactor leads to the following changes in the variation in the NO_2 concentration. The nitrogen dioxide concentration falls from 210 ppm by 106 ppm to 102 ppm in 286 s. Thereafter, the measurement values increase again comparatively slowly. In the 2nd and 3rd experiments with 0.4 g N,N'-dimethylurea, values of 101 ppm and 102 ppm respectively result for the decrease in nitrogen dioxide. All the results are again summarised in Table 16.

Table 16: Summary of the decrease in the NO_2 concentration

	0.4 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	286	-106
Experiment no. 2	320	-101
Experiment no. 3	334	-102

Increasing the amount of the substance to 0.7 g produced no significant increase in the values for the decrease in nitrogen dioxide compared with the experiments with 0.4 g. It was found that the nitrogen dioxide concentration decreases by 105 ppm over a period of

675 s. The results of the two repeat experiments, in addition to this result, are also shown in Table 17.

Table 17: Summary of the decrease in the NO_2 concentration

	0.7 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	675	-105
Experiment no. 2	725	-108
Experiment no. 3	716	-111

To be able also to investigate possible influences of carbon monoxide, three experiments were carried out with 0.1 g N,N'-dimethylurea and a carbon monoxide/nitrogen oxide mixture. Compared with the measurement without carbon monoxide, as in the two repeat experiments, there are no striking changes. Table 18 summarizes the results with and without carbon monoxide.

Table 18: Summary of the decrease in nitrogen dioxide without and with carbon monoxide

	0.1 g N,N'-dimethylurea (without CO)		0.1 g N,N'-dimethylurea (with CO)	
	Period [s]	NO_2 [ppm]	Period [s]	NO_2 [ppm]
Experiment no. 1	465	-48	492	-39
Experiment no. 2	497	-40	550	-46
Experiment no. 3	506	-38	532	-40

Interpretation of the results:

When N,N'-dimethylurea is heated above the melting point, ammonia probably forms and reduces some of the nitrogen dioxide by homogeneous gas phase reactions. If the results are compared with those which were achieved in the experiments with urea, it becomes clear that the

action is poorer if N,N'-dimethylurea is used, apart from the experiments with an amount of the substance of 0.1 g. As with N-formylurea, the poorer values for the nitrogen dioxide degradation are related to the higher molecular weight and the smaller amount of ammonia thus formed on heating. The better values compared with the experiments with an amount of substance of 0.1 g possibly result from a positive influence of the two methyl groups. This may also be the reason why the values for the nitrogen dioxide degradation are greater compared with those of the experiments with N-formylurea.

Influence of N,N'-dimethylurea on the nitrogen oxide concentrations:

The influence on the nitrogen oxide concentrations by vaporization of 0.1 g N,N'-dimethylurea was investigated. No changes were found in nitrogen monoxide compared with the normal concentration course. In contrast, the content of nitrogen dioxide is decreased by 48 ppm in 465 s. After this decrease, the values for the nitrogen dioxide concentration remain virtually constant to the end of the measurement. All the results of the three experiments with 0.1 g N,N'-dimethylurea are shown in Table 19. The results of the repeat experiments show no substantial differences from the first experiment here.

Table 19: Summary of the decrease in the NO_2 concentration

	0.1 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	465	-48
Experiment no. 2	497	-40
Experiment no. 3	506	-38

The vaporization of 0.4 g N,N'-dimethylurea in the reactor leads to changes in the variation in NO_2 concentration. The nitrogen dioxide concentration falls from 210 ppm by 106 ppm to 102 ppm in 286 s. Thereafter, the measurement values increase again comparatively slowly. In the 2nd and 3rd experiments with 0.4 g N,N'-dimethylurea, values of 101 ppm and 102 ppm respectively are obtained for the decrease in nitrogen dioxide. All the results are again summarized in Table 20.

Table 20: Summary of the decrease in the NO_2 concentration

	0.4 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	286	-106
Experiment no. 2	320	-101
Experiment no. 3	334	-102

Increasing the amount of the substance to 0.7 g produced no significant increase in the values for the decrease in nitrogen dioxide compared with the experiments with 0.4 g. The nitrogen dioxide concentration decreases by 105 ppm over a period of 675 s. The results of the two repeat experiments, in addition to this result, are also shown in Table 21.

Table 21: Summary of the decrease in the NO_2 concentration

	0.7 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	675	-105
Experiment no. 2	725	-108
Experiment no. 3	716	-111

To be able also to investigate possible influences of carbon monoxide, three experiments were carried out with 0.1 g N,N'-dimethylurea and a carbon monoxide/nitrogen oxide mixture. Compared with the measurement without carbon monoxide, as in the two repeat experiments, there are no striking changes. Table 22 summarizes the results with and without carbon monoxide.

Table 22: Summary of the decrease in nitrogen dioxide without and with carbon monoxide

	0.1 g N,N'-dimethylurea (without CO)		0.1 g N,N'-dimethylurea (with CO)	
	Period [s]	NO_2 [ppm]	Period [s]	NO_2 [ppm]
Experiment no. 1	465	-48	492	-39
Experiment no. 2	497	-40	550	-46
Experiment no. 3	506	-38	532	-40

Interpretation of the results:

When N,N'-dimethylurea is heated above its melting point, ammonia probably forms and reduces some of the nitrogen dioxide by homogeneous gas phase reactions. If the results are compared with those which were achieved in the experiments with urea, it becomes clear that the action is poorer if N,N'-dimethylurea is used, apart from the experiments with an amount of the substance of 0.1 g. As with N-formylurea, the poorer values for the nitrogen dioxide degradation are related to the higher molecular weight and the smaller amount of ammonia thus formed on heating. The better values compared with the experiments with an amount of substance of 0.1 g possibly result from a positive influence of the two methyl groups. This may also be the reason why the values for the nitrogen dioxide degradation are higher compared with those of the experiments with N-formylurea.

Influence of N,N-dimethylurea on the nitrogen oxide concentrations

A reduction in the nitrogen dioxide concentration by 46 ppm was achieved by vaporization of 0.1 g N,N-dimethylurea. It decreases from 102 ppm to 66 ppm in 690 s, and then rises again slightly. N,N-Dimethylurea

evidently has no influence on the nitrogen monoxide. Experiments nos. 2 and 3 give results which are in agreement. All the results of the three experiments are summarized in table 23.

Table 23: Summary of the decrease in the NO_2 concentration

	0.1 g N,N-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	690	-46
Experiment no. 2	650	-40
Experiment no. 3	690	-42

0.4 g N,N-dimethylurea had the effect of doubling the values for the decrease in nitrogen dioxide in a shorter period of time compared with the experiments with 0.1 g. The results of the three experiments carried out are summarized in Table 24.

Table 24: Summary of the decrease in the NO_2 concentration

	0.4 g N,N-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	285	-87
Experiment no. 2	285	-91
Experiment no. 3	285	-96

A further decrease in the NO_2 concentration could be achieved with 0.7 g N,N-dimethylurea. The NO_2 content decreases by 101 ppm in 330 s. The corresponding values of the two repeat experiments are shown in Table 25.

Table 25: Summary of the decrease in nitrogen dioxide

	0.7 g N,N-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	330	-101
Experiment no. 2	320	-105
Experiment no. 3	300	-104

Interpretation of the results:

The results of the experiments with N,N'-dimethylurea and N,N-dimethylurea are very similar. Consequently, the different arrangement of the methyl groups on the urea does not have such great importance. The explanation of the results is analogous to that for the experiments with N,N'-dimethylurea.

Influence of sulphur on the nitrogen oxide concentrations:

By employing 0.05 g sulphur, a decrease in the nitrogen dioxide concentration by 20 ppm and an increase in the nitrogen monoxide concentration by 9 ppm take place within 355 s. Thereafter, the nitrogen dioxide increases again slowly due to oxidation of the nitrogen monoxide, which decreases as a result. The two repeat experiments lead to results which are in agreement, as shown in Table 26.

Table 26: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.05 g sulphur		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	355	+9	-20
Experiment no. 2	360	+10	-19
Experiment no. 3	345	+8	-22

In an experiment with 0.1 g sulphur, slightly different values for the NO increase and the NO_2 decrease result compared with the experiment with 0.05 g sulphur. Over a period of 375 s, the nitrogen dioxide concentration decreases by 30 ppm and the nitrogen monoxide concentration increases by 10 ppm. These values are confirmed by Experiments nos. 2 and 3. The results of all the measurements with 0.1 g sulphur are shown in Table 27.

Table 27: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.1 g sulphur		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	375	+10	-30
Experiment no. 2	360	+10	-30
Experiment no. 3	360	+11	-32

The nitrogen dioxide concentration could be lowered still further with an amount of sulphur of 0.15 g, but the nitrogen monoxide concentration also rose somewhat. The nitrogen dioxide content decreases by 39 ppm within 370 s, while the nitrogen monoxide content increases by 21 ppm. The two repeat experiments produce corresponding results, which are also shown in Table 28.

Table 28: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.15 g sulphur		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	370	+21	-39
Experiment no. 2	420	+28	-40
Experiment no. 3	410	+22	-41

Three experiments were additionally also carried out with 0.1 g sulphur and a carbon monoxide/nitrogen oxide mixture. As can be seen from Table 29, no effect of the carbon monoxide on the results can be detected. The nitrogen dioxide concentration decreases by 31 ppm in 390 s and the nitrogen monoxide concentration increases by 10 ppm.

Table 29: Increase and decrease respectively in the concentrations of NO and NO_2 with and without CO

	0.1 g sulphur (without CO)			0.1 g sulphur (with CO)		
	Period [s]	NO [ppm]	NO_2 [ppm]	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	375	+10	-30	390	+8	-31
Experiment no. 2	360	+10	-30	425	+10	-32
Experiment no. 3	360	+11	-32	410	+14	-33

Interpretation of the results:

Sulphur self-ignites at approx. 260°C and burns with a weak blue flame to give sulphur dioxide and up to 40% sulphur trioxide. Below 300°C, NO_2 reacts directly with SO_2:

$$NO_2 + SO_2 \rightarrow NO + SO_3$$

In addition to sulphur trioxide, nitrogen monoxide is also formed in this reaction, and can probably also react with sulphur dioxide:

$$2\ NO + SO_2 \rightarrow N_2O + SO_3$$

This equation would also explain why NO does not increase at the rate at which NO_2 is degraded.

Claims:

1. Process for the reduction of harmful gases in gas mixtures from pyrotechnic reactions, characterized in that at least one additive from the group consisting of metallocenes, metallocene derivatives, urea, urea derivatives, sulphur and/or sulphur compounds is vaporized during the pyrotechnic reaction by the heat generated in the pyrotechnic reaction and the harmful gases are converted into non-toxic compounds in a homogeneous gas phase reaction.

2. Process for the reduction of harmful gases in gas mixtures from pyrotechnic reactions according to claim 1, characterized in that the additive chosen has a melting point > 105°C and vaporizes below 400°C.

3. Process for the reduction of harmful gases in gas mixtures from pyrotechnic reactions according to claim 1 or 2, characterized in that ferrocene, 1,1'-diacetylferrocene, titanocene pentasulphide, urea, N-formylurea, N,N'-dimethylurea, N,N-dimethylurea and/or sulphur, preferably ferrocene, is employed as the additive.

4. Agent for pyrotechnic gas generation, characterized in that, in addition to the gas-generating substance, it comprises an additive from the group consisting of metallocenes, metallocene derivatives, urea, urea derivatives, sulphur and/or sulphur compounds which vaporizes due to the heat generated in the pyrotechnic reaction.

5. Agent for pyrotechnic gas generation according to

claim 4, characterized in that the additive chosen has a melting point > 105°C and vaporizes below 400°C.

6. Agent for pyrotechnic gas generation according to claim 4 or 5, characterized in that ferrocene, 1,1'-diacetylferrocene, titanocene pentasulphide, urea, N-formylurea, N,N'-dimethylurea, N,N-dimethylurea and/or sulphur, preferably ferrocene, is employed as the additive.

7. Agent for pyrotechnic gas generation according to one of claims 4 to 6, characterized in that at least one component of the gas-generating substance is coated with the additive.

8. Device for pyrotechnic gas generation, characterized in that at least one additive from the group consisting of metallocenes, metallocene derivatives, urea, urea derivatives, sulphur and/or sulphur compounds is introduced into the flow path of the working gas.

9. Device for pyrotechnic gas generation, characterized in that the additive chosen has a melting point > 105°C and vaporizes below 400°C.

10. Device for pyrotechnic gas generation, characterized in that ferrocene, 1,1'-diacetylferrocene, titanocene pentasulphide, urea, N-formylurea, N,N'-dimethylurea, N,N-dimethylurea and/or sulphur, preferably ferrocene, is employed as the additive.

Abstract:

The present invention provides for the reduction of harmful gases in gas mixtures from pyrotechnic reactions.

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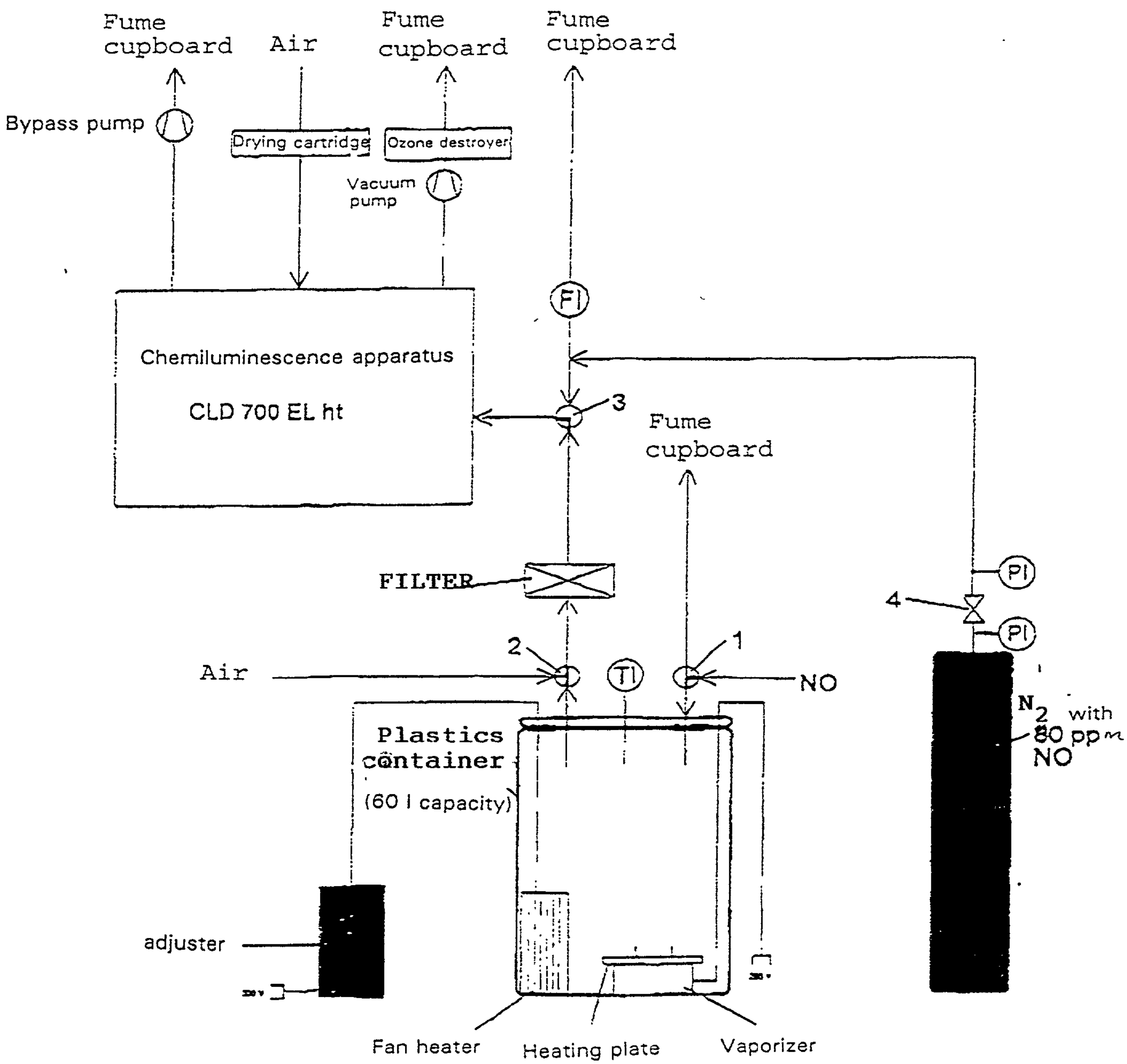

Figure 1: Process flow scheme of experimental apparatus

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DECLARATION AND POWER OF ATTORNEY FILED WITH U.S. DESIGNATED OFFICE UNDER 35 U.S.C. 371(c)(4)

As a below named inventor, I/we hereby declare that:

My/Our residence, post office address and citizenship are as stated below next to my/our name, I/we believe that I/we are the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Reduction Of Noxious Gases In Gas Mixtures From Pyrotechnic Reactions

_______________________________________,

the specification of which was filed as PCT International Application No. PCT/EP98/02562 US Serial No. 09/423,086

filed April 30, 1998 and was amended on _______________.
(if applicable)

I/We hereby state that I/we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I/We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I/We hereby claim benefit under Title 35, United States Code, §119 of any provisional application(s) and any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the foreign application(s) on which priority is claimed:

Provisional and/or Foreign Application(s)

(Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed: Yes	Priority Claimed: No
197 18 553.3	Germany	2/5/97	[X]	[ ]
			[ ]	[ ]
			[ ]	[ ]
			[ ]	[ ]
			[ ]	[ ]
			[ ]	[ ]

I/We hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I/we acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT internatinal filing date of this application:

(Application Serial No.)	(Filing Date)	(Status: patented, pending, abandoned)

(Continued on Page 2)

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I hereby appoint ~~as~~ principal attorneys; Donald R. Antonelli, Reg. No. 20,296; David T. Terry, Reg. No. 20,178; Melvin Kraus, Reg. No. 22,466; William I. Solomon, Reg. No. 28,565; Gregory E. Montone, Reg. No. 28,141; Ronald J. Shore, Reg. No. 28,577; Donald E. Stout, Reg. No. 26,422; Alan E. Schiavelli, Reg. No. 32,087; James N. Dresser, Reg. No. 22,973 and Carl I. Brundidge, Reg. No. 29,621 to prosecute and transact all business connected with this application and any related United States application and international applications. Please direct all communications to the following address:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United State Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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